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# Quantized non-adiabatic coupling terms to ensure diabatic potentials

Michael Baer [a,b,*,1], Alexander Alijah [c,d,2]

[a] *Institute of Atomic and Molecular Science, Tiape, 10764, Taiwan*
[b] *Department of Physics and Applied Mathematics, Soreq NRC, Yavne 81800, Israel*
[c] *Department of Chemistry, The University of Coimbra, P-3049 Coimbra Codex, Portugal*
[d] *Department of Chemistry, Bielefeld University, Bielefeld, Germany*

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**Abstract**

A way to derive rigorous diabatic potentials from non-adiabatic coupling terms (NACTs) was suggested some time ago [M. Baer, Chem. Phys. Lett. 35 (1975) 112]. This approach could be applied only for cases when the NACTs are regular throughout configuration space. In this work a criterion is established to be fulfilled by NACTs which yields continuous and uniquely diabatic potentials defined throughout configuration space. It is found that this requirement leads to a kind of 'quantization' with regard to the non-regular NACTs. A two-state model and a three-state model were considered as examples. © 2000 Elsevier Science B.V. All rights reserved.

## 1. Introduction

Recently we studied three-state systems with the aim of revealing geometrical effects [1,2]. These studies were of two kinds:

(a) In the first [1] we started with a diabatic potential matrix (expressed in terms of two coordinates $q$ – the radial coordinate – and $\varphi$ – the angular coordinate defined along the range $\{0, 2\pi\}$), calculated the non-adiabatic coupling terms (NACTs; using the Hellmann–Feynman theorem) and following that, employed the Top–Baer [3] equations to calculate the three adiabatic-to-diabatic transformation (ADT) angles which constitute the ADT matrix. We found that all three angles attain, following a full cycle, the values $\pi$ or zero, somewhat reminiscent of the 'Berry' phase in the two-state case. These calculations were repeated for a whole range of parameters that define the diabatic potential matrix and we always got the same *kind* of results.

(b) In a different study [2] we tried to construct a $3\times 3$ diabatic potential matrix by assuming three *adiabatic* potentials $u_j$; $j=1,2,3$ and three (vectorial) NACTs $t_j$, $j=1,2,3$ (each $3\times 3$ non-adiabatic coupling matrix $\boldsymbol{\tau}$ can have at most three different (vectorial) terms). We found that arbitrary choices of the NACTs cannot lead to a single-valued diabatic *potential* matrix.

* Corresponding author. Fax: +972-8-9434157; e-mail: mmbaer@netvision.net.il

[1] Guest Professor at the Institute of Atomic and Molecular Science, Taipe, Taiwan.

[2] Guest Professor at the University of Coimbra, P-3049 Coimbra Codex, Portugal.

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In this Letter a theory is presented which shows that these two findings are inter-related and lead to important consequences regarding features of the $\boldsymbol{\tau}$-matrix elements.

In Section 2 the ADT matrix $\mathbf{A}$ is introduced with the diabatic representation, in Section 3 necessary conditions to be satisfied by $\mathbf{A}$ in order to guarantee a well-defined diabatic framework are discussed, in Section 4 analytical examples are worked out, and in Section 5 the conclusions are summarized.

## 2. Adiabatic–diabatic transformation (ADT) matrix

It was shown that in order to eliminate the NACTs from the Schrödinger equation (SE), the ADT matrix $\mathbf{A}$ has to fulfill the following first order-vector equation [4,5].

$$\nabla\mathbf{A} + \boldsymbol{\tau}\mathbf{A} = 0\,. \tag{1}$$

It was then suggested that a convenient way to treat this 'simultaneous' set of differential equations is to convert Eq. (1) into an integral equation along a line [4,6,7], namely:

$$\mathbf{A}(s, s_0) = \mathbf{A}(s_0) - \int_{s_0}^{s} \mathrm{d}s'\, \boldsymbol{\tau}(s')\mathbf{A}(s', s_0)\,, \tag{2}$$

where $s$ and $s_0$ are two points in configuration space (CS), the matrix $\mathbf{A}(s_0)$ is a boundary condition and the dot stands for a scalar product between the vector matrix $\boldsymbol{\tau}$ and the differential path element $\mathbf{d}\boldsymbol{s}$. It is understood that the integration is performed along a line $\Gamma$ that combines $s$ and $s_0$, thus $\Gamma = \Gamma(s, s_0)$. Eq. (2) can also be written in a more convenient way as [6,7]:

$$\mathbf{A}(s, s_0) = \mathbf{A}(s_0) - \int_{s_0}^{s} \tau_s(s')\mathbf{A}(s', s_0)\,\mathrm{d}s'\,, \tag{2'}$$

where $\tau_s$ is the component of $\boldsymbol{\tau}$ along $\Gamma$. In general one would expect, for a given set of points, $(s, s_0)$, different results for different paths.

Once having $\mathbf{A}(s, s_0)$ we are in the position to calculate the diabatic potential matrix, $\mathbf{W}(s, s_0)$, which is given in the form [4]:

$$\mathbf{W}(s, s_0) = \mathbf{A}^{\dagger}(s, s_0)\,u(s)\mathbf{A}(s, s_0)\,, \tag{3}$$

where $u(s)$ is the adiabatic potential matrix and $\mathbf{A}^{\dagger}(s, s_0)$ is the complex conjugate matrix of $\mathbf{A}(s, s_0)$. It is well noticed that as long as $\mathbf{A}(s, s_0)$ is uniquely defined at each point the same holds for $\mathbf{W}(s, s_0)$. The question is whether is it really necessary for $\mathbf{A}(s, s_0)$ to be single-valued in order to ensure a single-valued $\mathbf{W}(s, s_0)$? The answer to this question is "No" as will be shown in Section 3.

## 3. Necessary conditions for having a uniquely defined diabatic potential matrix

To prove our claim we have to go, mathematically, the backwards direction, namely assuming that $\mathbf{W}(s, s_0)$ is uniquely defined and obtain the features to be fulfilled by $\mathbf{A}(s, s_0)$.

To this effect we introduce a closed path $\Gamma$ defined in terms of a continuous parameter $\lambda$ so that the starting point $s_0$ of the path is for $\lambda = 0$. Next we define $\beta$ as the value attained by $\lambda$, once the path completes a full cycle and reaches its starting point. Thus, for instance, in the case of a circle, $\beta = 2\pi$.

Having introduced these definitions we can now express our assumption regarding the uniqueness of $\mathbf{W}(s, s_0)$ in the following way: At *each point* $s_0$ in CS the diabatic potential matrix $\mathbf{W}(\lambda)$ ($\equiv \mathbf{W}(s(\lambda), s_0)$) fulfills the relation:

$$\mathbf{W}(\lambda = 0) = \mathbf{W}(\lambda = \beta)\,. \tag{4}$$

Following Eq. (3) this requirement implies that for every point $s_0$ we have:

$$\mathbf{A}^{\dagger}(0)\,u(0)\mathbf{A}(0) = \mathbf{A}^{\dagger}(\beta)\,u(\beta)\mathbf{A}(\beta)\,. \tag{5}$$

By definition we have that $u(0) \equiv u(\beta)$ and therefore:

$$u(0) = \mathbf{B}^{\dagger}(\beta)\,u(0)\mathbf{B}(\beta)\,, \tag{6}$$

where for any $\lambda$, $\mathbf{B}(\lambda)$ is defined as

$$\mathbf{B}(\lambda) = \mathbf{A}(\lambda)\mathbf{A}^{\dagger}(0)\,. \tag{7}$$

From Eq. (6) one can show (by considering Eq. (6) as a set of linear algebraic equations for the 'unknown' adiabatic potentials – $u_j(0)$) that if $b_{jk}$ is the $(j, k)$th matrix element of $\mathbf{B}(\lambda)$ at $\lambda = \beta$ the following relation holds

$$(b_{jk})^{*}\, b_{jk} = \delta_{jk}\,; \quad j, k = 1, \ldots, N\,, \tag{8}$$

or

$$b_{jk} = \delta_{jk} \exp(i\chi_k) . \quad (9)$$

Thus $\mathbf{B}(\beta)$ is a diagonal matrix which contains in its diagonal complex numbers whose norm is 1.

Recalling Eq. (7) we get that:

$$\mathbf{A}(\beta) = \mathbf{B}(\beta)\mathbf{A}(0) . \quad (10)$$

It is noticed that if $\mathbf{A}(\lambda)$ is calculated along a closed path and the end point $\lambda = \beta$ is identical to the initial point $\lambda = 0$ then $\mathbf{A}(\beta)$ is not necessarily identical to $\mathbf{A}(0)$, namely $\mathbf{A}(\lambda)$ does not have to be uniquely defined at every point in CS, in order to be able to produce single-valued diabatic potentials.

To prove that $\mathbf{A}(\beta)$ as presented in Eq. (10) yields a uniquely defined diabatic matrix $\mathbf{W}(\lambda)$ we have to show that this matrix fulfills Eq. (5). Thus replacing in Eq. (5), the matrix $\mathbf{A}(\beta)$ by the product $\mathbf{B}(\beta)\mathbf{A}(0)$ and recalling that both $u(\beta)$ and $B(\beta)$ are diagonal matrices the equality is, indeed, guaranteed.

We shall summarize the discussion presented so far: It was shown that in order for a diabatic *potential* matrix of the kind given in Eq. (3), to be single-valued, the ADT matrix has to fulfill, at *every* point in CS, the conditions as specified by Eqs. (9) and (11). These conditions are less stringent then demanding that the ADT matrix has to be uniquely defined throughout CS.

## 4. Application for some special cases

The examples that will be discussed here are for systems with two polar coordinates $(q, \varphi)$, where the non-adiabatic coupling elements are of the form:

$$\tau_{jk} = q^{-1}\boldsymbol{\sigma}_{jk} . \quad (11)$$

Here $\boldsymbol{\sigma}_{jk}$ is the $(j, k)$ element of a *constant* matrix $\boldsymbol{\sigma}$. Employing Eq. (1), the non-adiabatic coupling elements for this model can be derived analytically. A straightforward integration of Eq. (1) for a fixed value of $q$ leads to the following representation of $\mathbf{A}(\varphi)$:

$$\mathbf{A}(\varphi) = \exp(-\boldsymbol{\sigma}\varphi)\mathbf{A}(\varphi = 0) , \quad (12)$$

which can be shown to be of the form:

$$\mathbf{A}(\varphi) = \mathbf{G}^{\dagger}\mathbf{E}(\varphi)\mathbf{G}\mathbf{A}(\varphi = 0) . \quad (13)$$

Here $\mathbf{G}$ is a unitary matrix that diagonalizes $\boldsymbol{\sigma}$, and $\mathbf{E}(\varphi)$ is a diagonal matrix that contains elements of the type $\exp(g_k\varphi)$, where $g_k$ $(k = 1, \ldots, N)$ are the eigenvalues of $\boldsymbol{\sigma}$. Next we derive $\mathbf{B}(\varphi = 2\pi)$ which follows from Eqs. (13) and (11). It can be seen that:

$$\mathbf{B}(\varphi = 2\pi) = \exp(-2\pi\boldsymbol{\sigma}) = \mathbf{G}^{\dagger}\mathbf{E}(\varphi = 2\pi)\mathbf{G} , \quad (14)$$

where $\mathbf{B}(\varphi = 2\pi)$ has to be a diagonal matrix (see Eq. (9)). This fact imposes limitations on the allowed values of the eigenvalues of the $\boldsymbol{\sigma}$-matrix and in this sense it can be considered as a *quantization* process. The relevance of this statement will be clarified while studying the next two examples.

### 4.1. Two-state system

In this case the $\boldsymbol{\sigma}$-matrix is of the form:

$$\boldsymbol{\sigma} = \begin{pmatrix} 0 & t \\ -t & 0 \end{pmatrix} , \quad (15)$$

where $t$, at this stage, is an arbitrary constant (this example can be easily extended to the case that $t$ is a general function). The matrix $\mathbf{G}$ that diagonalizes $\boldsymbol{\sigma}$ is of the form:

$$\mathbf{G} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 1 \\ \mathrm{i} & -\mathrm{i} \end{pmatrix} , \quad (16)$$

and the corresponding eigenvalues are $\pm \mathrm{i}t$. Following Eq. (14) we get for the matrix $\mathbf{B}(\varphi = 2\pi)$ the result:

$$\mathbf{B}(\varphi = 2\pi) = \begin{pmatrix} \cos(2\pi t) & -\sin(2\pi t) \\ \sin(2\pi t) & \cos(2\pi t) \end{pmatrix} . \quad (17)$$

It is noticed that in order for $\mathbf{B}(\varphi = 2\pi)$ to be diagonal the $t$-values have to be $t = n/2$, where $n$ is an integer. Following the discussion in the previous section this result implies that the *only* constants $t$, capable of yielding a *continuous uniquely* defined diabatic potential matrix, are those that fulfill $t = n/2$ with $n$ being an integer. The case $n = 1$ is the well-known conical intersection case.

The diabatic potential matrix for the conical intersection was derived by Baer and Englman [8] and later applied for a scattering model calculation by Baer et al. [9] and by Adhikari and Billing [10]. The transition probabilities due to the diabatic potentials

that were formed following the ADT were similar to those obtained from other treatments, in particular the one due to Kuppermann et al. approach which utilizes asymmetrical $\varphi$-dependent basis sets [10–12].

We summarize what has been shown in this example: The $\boldsymbol{\tau}$-matrix presented in Eqs. (11) and (15), is regular for any $t$-value at every point in CS except at the origin. This singularity led to a non-unique ADT matrix but not necessarily to a non-uniquely defined diabatic potential matrix. It is true that for a general $t$-value also this matrix will be multi-valued, however, single-valued diabatic potential matrices will be formed, if and only if $t = n/2$, where $n$ is an integer. This is can be considered as a kind of *quantization* of the eigenvalues of the non-adiabatic coupling matrix in the case of a two-state system.

### *4.2. Three-state system*

Within the three-state case we distinguish between four types of $\boldsymbol{\sigma}$-matrices. We could study the general case but, here, for the sake of simplicity, we shall consider only the case where non-zero couplings are assumed between consecutive states, namely, between the first and the second state and between the second and the third state. Thus:

$$\boldsymbol{\sigma} = \begin{pmatrix} 0 & t_1 & 0 \\ -t_1 & 0 & t_2 \\ 0 & -t_2 & 0 \end{pmatrix}, \tag{18}$$

where $t_1$ and $t_2$ are arbitrary constants. The matrix $\mathbf{G}$ that diagonalizes $\boldsymbol{\sigma}$ is of the form:

$$\mathbf{G} = \frac{1}{\varpi\sqrt{2}} \begin{pmatrix} t_1 & t_1 & t_2\sqrt{2} \\ \mathrm{i}\varpi & -\mathrm{i}\varpi & 0 \\ -t_2 & -t_2 & t_1\sqrt{2} \end{pmatrix}, \tag{19}$$

where $\varpi$ is defined as $\varpi = \sqrt{t_1^2 + t_2^2}$ and the three eigenvalues are: $(0, \pm \mathrm{i}\varpi)$. Following Eq. (14) we get for $\mathbf{B}(\varphi = 2\pi)$ the expression:

$$\mathbf{B}(\varphi = 2\pi) = \varpi^{-2} \begin{pmatrix} t_2^2 + t_1^2 c_1 & t_1 \varpi s_1 & 2 t_1 t_2 s_2 \\ t_1 \varpi s_1 & (t_1^2 + t_2^2) c_1 & -t_2 \varpi s_1 \\ 2 t_1 t_2 s_2 & t_2 \varpi s_1 & t_1^2 + t_2^2 c_1 \end{pmatrix}, \tag{20}$$

where

$$c_1 = \cos(2\pi\varpi); \quad s_1 = \sin(2\pi\varpi); \quad s_2 = \sin^2(\pi\varpi).$$

It is noticed that in order for $\mathbf{B}(\varphi = 2\pi)$ to be diagonal, $\varpi$ has to fulfill the following 'quantization' condition:

$$\varpi = n \;\rightarrow\; t_1^2 + t_2^2 = n^2, \tag{21}$$

where $n$ is an integer. It is also noticed that in this case $\mathbf{B}(\varphi = 2\pi)$ becomes a unit matrix. Thus uniquely defined diabatic potential matrices are guaranteed if and only if $t_1$ and $t_2$ fulfill Eq. (21), which like the previous case, is reminiscent of a quantization process (we recall that $\pm\varpi$ (or $\pm\mathrm{i}\varpi$) are the eigenvalues of $\boldsymbol{\sigma}$).

## 5. Conclusions

In this work we have established a criterion to construct models for non-adiabatic coupling matrices that will yield uniquely define diabatic potentials. It was known for quite some time that employing Eqs. (1)–(3), as such, for forming diabatic potentials may encounter difficulties believed to be associated with the non-completeness of a partial set of a Hilbert space. This belief led Mead and Truhlar [13] as far as to say that diabatic potentials do not exist ''except in the trivial sense of letting the sum run over a *complete set* of electronic states ...'' [14], and caused many other researchers in the field to follow in their foot steps [15,16]. But there are also other opinions [17–19]. In particular Pacher et al. [18] showed that solving Eq. (1) is equivalent to using the propagative block diagonalization procedure which they applied successfully for ab initio calculations. It is true that in many cases diabatic states cannot be formed but to go as far saying they do not exist and therefore Eqs. (1)–(3) are of no use, is misleading. Also, the completeness difficulty as discussed by Mead and Truhlar [13] can be overcome employing projection operators [20]. To some extent this difficulty was treated by Pacher et al. who discussed conditions where the completeness of the Hilbert space does not prevent the application of Eqs. (1)–(3) [19,21].

In the present study we derived, employing Eqs. (1)–(3), the necessary conditions to be fulfilled by the non-adiabatic coupling matrices in order to yield uniquely defined diabatic potentials. Moreover we

considered two models – a two-state model and a three-state model – to show that rigorously diabatic potentials can be formed but only for a particular choice of parameters that define the non-adiabatic coupling terms. This 'particular choice' of parameters is reminiscent of a *quantization* process applied to the parameters that define the non-adiabatic coupling terms. These ideas are now extended to more general cases and will be considered elsewhere [20].

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